IMPROVEMENT OF H_2O_2 STABILIZATION IN RAINWATER SAMPLES

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ABSTRACT

Peroxides collected in rainwater readily decompose in the natural matrix, consequently it is hard to estimate their values present during precipitation events. For this reason, only few data concerning the concentration of aqueous H_2O_2 in dew, cloud and rainwater are available. Therefore, it is necessary to establish a sampling protocol under conditions that assure the real-time estimation of hydrogen peroxide in rainwater samples. Hydrogen Peroxide was determined by a fluorometric method in rainwater collected in fives sites in Mexico. Measured levels for all sampled sites were in agreement with values reported by other authors for marine and continental sites. To establish a sampling protocol, several methods reported for preservation of H_2O_2 in rainwater were assessed. Sampling protocol proposed in this research involves forming fluorescent dimmer on-site immediately after sample collection, and storing at dark and 4 ºC. This procedure gives a 10 days margin to perform sample analysis, guarantying a minimal decomposition of H_2O_2 in rainwater samples (approximately 10%) and allowing more time to perform sampling campaigns even in remote sites. The other methods evaluated (freezing, filtering, using acidified samplers, adding sodium stannate, and storing samples and their fluorescent dimmer at 0ºC) do not exert any preservation effect over H_2O_2 levels in rainwater samples.

INTRODUCTION

The contribution of NO_3^- and SO_4^{2-} to acidity of rainwater has become one of the main environmental problems, and it has been subject of numerous researches (Pierson and Chang, 1986; O'Sullivan, 1985; Hansen and Hidy, 1982; Beilke, 1983; Dikaiakos *et al.*, 1990; Bravo *et al*, 2000; Cerón *et al.*, 2002). Reasons to use SO_4^{2-} ion as the main indicator of acidity, are: 1) its conservative character, 2) there is no a variation in its levels among remote sites, and 3) do not promote acidification in a short time period as

the case of NO_3^- (Báez and Belmont, 1987; Báez *et al.*, 1993; Báez *et al.*, 1997a; Báez *et al.*, 1997b; Bravo *et al.*, 2000; Cerón *et al.*, 2002).

There are several oxidants in the atmosphere that play an important role in the conversion of SO_2 to H_2SO_4. In aqueous phase, there are two main routes for SO_2 oxidation: if rainwater pH is greater than 5, O_3 acts as the principal oxidant. On the other hand, if rainwater pH is minor than 4.5, H_2O_2 contributes in a great proportion to the acidification process (Zika *et al.*, 1982; Chameides, 1984; Calvert *et al.*, 1985; Sakugawa *et al.*, 1993; Sauer *et al.*, 1997). H_2O_2 is very important in the oxidation process of S(IV) in aqueous phase, then it is necessary to characterize its levels present in air, cloud water and rainwater. Specifically, measurement of hydrogen peroxide concentrations in water droplets can afford an estimation of the gas phase concentration and oxidation rate of sulphur dioxide.

Until now, not many information on the concentration of atmospheric aqueous H_2O_2 is available, where several interferences associated with the sampling procedure for H_2O_2 in gaseous phase have been reported (Cohen *et al.*, 1967; Possanzini *et al.*, 1988; Sakugawa and Kaplan, 1993). However, some works about determination of H_2O_2 content in rain and cloud water (Kok, 1980; Zika *et al.*, 1982; Cooper *et al.*, 1987; Sakugawa and Kaplan, 1987; Miller and Kester, 1994; Willey *et al.*, 1996; Sauer *et al.*, 1997; Deng and Zuo, 1999; Yuan and Shiller, 2000; Ortiz *et al.*, 2000), report H_2O_2 concentrations from 1 to 135 µM. Unfortunately, H_2O_2 present into water droplets readily decompose by a catalytic process that involves a great variety of metals (Kremer, 1985; Greadel *et al.*, 1986; Luñak and Sedlak, 1992; Zepp, 1992; Sedlak *et al.*, 1997). Ortiz *et al.* (2000) showed that substantial decomposition of H_2O_2 levels in rainwater and cloud water samples take place during the time elapsed between collection and analysis, time values reported fluctuate from 80 to 700 min. For this reason, in most of methods proposed for hydrogen peroxide analysis in rainwater, samples must be analyzed immediately after its collection, making very hard to estimate H_2O_2 levels that existed in the sampling moment.

Due to the scarce measurements of H_2O_2 in rainwater and the lack of confidence in gas phase measurements, most of the results reported have only a qualitative character until now, and it has

no been possible to find defined correlations or a tendency between data.

Hence, in order to assess quantitatively the process that control H_2O_2 atmospheric levels, more measurements of H_2O_2 in rainwater are required, specially, under a great variety of preservation conditions that minimize its rate of decomposition after collection and assure its proper determination.

On the other hand, some authors report that using fluorometric methods samples can be preserved during several days (Sakugawa and Kaplan, 1987; Sauer *et al.*, 1997), unfortunately, the conditions and the preservation time have not been well established.

As a result, the objective of this work was to determine H_2O_2 levels in rainwater, using different preservation methods, compare the results obtained in each one, and to establish a sampling protocol that assure its quantitative determination, even in remote sites. This result will permit in a subsequent stage of this research, to assess quantitatively the processes that control atmospheric H_2O_2 levels in gas and aqueous phase in marine, coastal and continental sites.

EXPERIMENTAL METHOD
Analytical Technique

A derivatization technique has been reported by several authors for the combined determination of hydrogen peroxide and some organic hydroperoxides in precipitation samples (Keuken *et al.*, 1988; Sakugawa and Kaplan, 1987; Olszyna *et al.*, 1988; Kelly *et al.*, 1985; Zika *et al.*, 1982; Lazrus *et al.*, 1985). This analytical technique combines the sensitivity of fluorometry with the specificity of enzymatic reactions. This fluorometric method allows the sensitive detection of hydrogen peroxide and organic peroxides in aqueous phase, through enzymatic catalysis and formation of fluorescent species, followed by the speciation of H_2O_2 and organic peroxides through a selective decomposition of H_2O_2 that is catalyzed by catalase enzyme.

The analytical procedure is based on the fluorescent detection of the dimmer obtained from the reaction between p-hydroxy-phenylacetic acid and H_2O_2 at pH 8.5, in the presence of peroxidase "horseradish". The dimmer is quantified by fluorescent detection using an excitation wavelength of 320 nm and measuring the emission intensity at 400 nm. This fluorescence is therefore, proportional to the H_2O_2 concentration. The specific detection is

performed through the destruction of H_2O_2 by catalase enzyme, and the difference between values obtained with (organic peroxides) and without catalase (total peroxides) gives the total H_2O_2 content (Lazrus *et al.*, 1985; Lazrus *et al.*, 1986; Kok *et al.*, 1986; Sakugawa and Kaplan, 1987).

A Spectra-system FL-3000 detector connected to an HPLC (high performance liquid chromatography) equipment with a single channel was used to measure hydrogen peroxide levels. Sample was loaded into a sample injection valve using a glass syringe with a Teflon plunger, injection system was modified to ensure that sample was injected directly to detector. Specific detection of H_2O_2 levels in a single channel detector involves manual addition of catalase and the analysis of two aliquots, thereby, more sample, chemical reagent and analysis time are required. Blank samples were made using pure water both with and without addition of catalase. The fluorescence for each blank value was subtracted from each sample value.

Two aliquots of 1.8 ml of sample were required. First sample aliquot or standard was transferred with a pipette to a 10 ml vial, then 0.3 ml of 0.1 M potassium hydrogen phthalate (pH 5.5) and EDTA (1×10^{-3} M) were added; Fluorescent reagent [0.3 ml of 1×10^{-2} M of p-hydroxyphenylacetic acid (Aldrich) and peroxidase (0.8 mg of 10 purpuro-gallin units ml^{-1} (Sigma))] were added to it. After 1 minute of reaction time, 0.3 ml of 0.2 M NaOH was added to stabilize the generated fluorescence. This procedure allows the determination of total peroxide (H_2O_2 and organic peroxide).

To discriminate H_2O_2 from organic peroxides, 0.3 ml of catalase reagent (500 unit ml^{-1}, Sigma) was added to the second sample aliquot (1.8 ml). After 40 seconds, fluorescent reagent with peroxidase (0.3 ml) was added. Finally, fluorescent reaction obtained was stabilized by adding NaOH 0.2 M. H_2O_2 is more rapidly decomposed by catalase than organic peroxides, and the difference in fluorescent signals obtained in both cases, with and without catalase, represents the total content of H_2O_2 in the rainwater sample or standard solution.

H_2O_2 standards were prepared by dilution of a stock H_2O_2 standard. H_2O_2 concentration of the stock standard solution was determined by titration with $KMnO_4$. A 10,000 μM H_2O_2 standard was prepared by dilution of commercially available 30% H_2O_2. Stock H_2O_2 solutions prepared in this manner are found to decay to a rate about 1% per month. Working standards were prepared daily. Glassware to be used in preparing H_2O_2 standards should be washed with soap, rinsed, and allowed to soak in deionised water for several days with frequent water changes. In analytical work with H_2O_2 it is important that all solutions be prepared from water free of bacteria as well as ionic impurities.

In this work, solutions were prepared with purified water by deionization cartridges and stored at dark and 4°C. Another important detail of the analysis procedure is to use freshly made fluorescent reagent (p-hydroxyphenylacetic acid + peroxidase enzyme). This reagent decomposes after some storing time, consequently results are altered and precision is lost. Differences in duplicate measurements were below 10%.

Concentrations above 15 μM H_2O_2 saturated photomultiplier tube, due to detector sensitivity, thus it was not possible to measure H_2O_2 levels directly. For that reason, in order to extend the calibration curve, it was indispensable to make dilutions. Effectiveness of this procedure was tested measuring 1:2, 1:5 and 1:10 dilutions of standard solutions and samples. Results showed that the best fitting is obtained with 1:10 dilution of fluorescent dimmer, consequently, reagents are saved and calibration curve is extended, allowing detection from 0.5 to 100 μM of H_2O_2 in rainwater. Detection limit of this analytical method was 0.5 μM of H_2O_2.

Sample Collection

Rainwater samples were collected in five sites in Mexico. Figure 1 comprises a map showing their geographical location: site one was positioned on the roof of the Atmospheric Sciences Centre Building in Mexico City; site two was placed on the roof of a residential site in Mexico City; site three was sited in a residential area in Orizaba City; site four was located at the top of a meteorological station located in Puerto Morelos Town; and site number five was positioned in Tropical Pacific Ocean on board of Oceanographic Ship "PUMA". In all cases, rainwater was collected using a 2 liters glass beaker, and the collectors were far from any possible emission source. Samples were transferred to glass bottles protected from light.
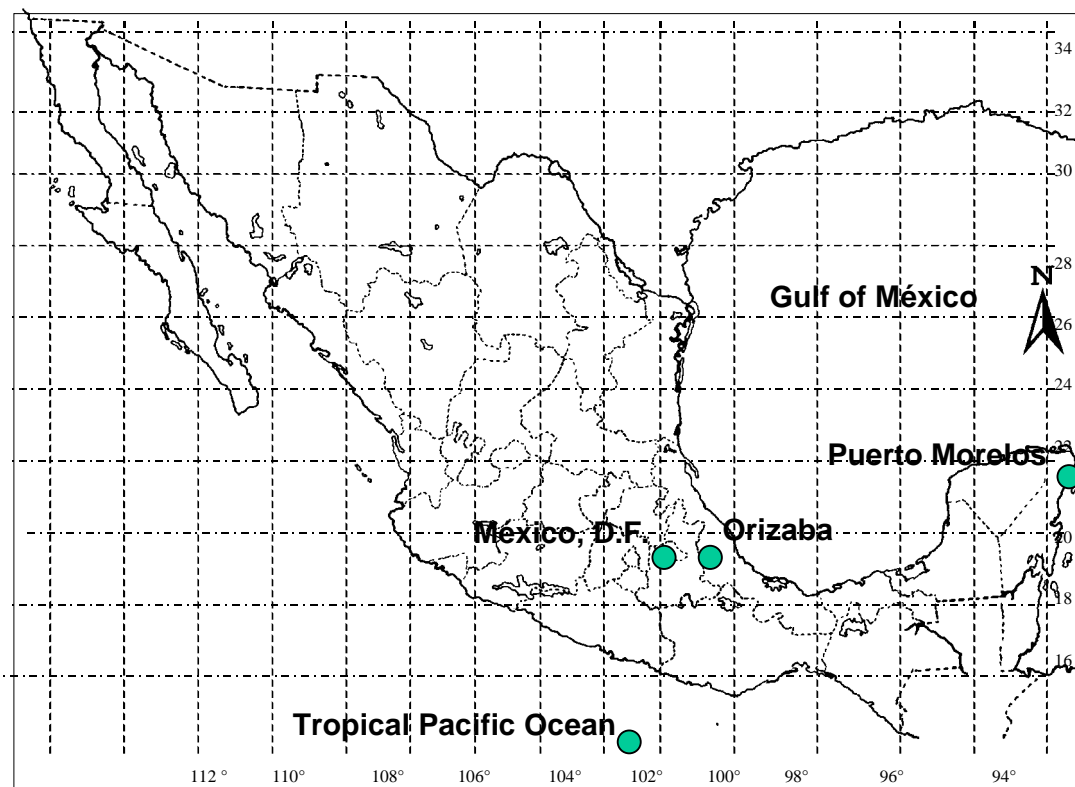
Figure 1 Sampling sites location: Orizaba City, México, D.F. City, Puerto Morelos Town, and Tropical Pacific Ocean

RESULTS AND DISCUSSION

A study with standard solutions and samples was performed to observe the decay of H_2O_2 levels after their preparation or collection, using different methods to preserve them. The methods evaluated to preserve H_2O_2 levels in rainwater samples were:

a) Freezing rainwater samples.
b) Filtering rainwater samples.
c) Using acidified rainwater samplers.
d) Adding sodium stannate to rainwater samples.
e) Storing samples and fluorescent dimmer at 0 and at 4ºC.

In all cases, it was observed that total peroxides were constituted by hydrogen peroxide, and organic peroxides fraction was not significant. On the other hand, the values obtained were of the same order of magnitude of marine, continental and coastal sites values reported by several authors (Kok, 1980; Zika *et al.*, 1982; Cooper *et al.*, 1987; Sakugawa and Kaplan, 1987; Miller and Kester, 1994; Willey *et al.*, 1996; Sauer *et al.*, 1997; Deng and Zuo, 1999; Yuan and Shiller, 2000). Some works (Kok, 1980; Deng and Zuo, 1999) suggest that storing

samples at 0ºC, makes possible to preserve them for H_2O_2 analysis. However, Sauer *et al.* (1997) found in samples stored at –18ºC, that hydrogen peroxide levels decrease 50%, after 6 hours of their collection.

From August 27 to September 27 of 2000, 43 samples were obtained at Puerto Morelos Town and preserved only by freezing. Results show an average H_2O_2 concentration of 7.7 μM, ranging from 0.5 to 28.13 μM and are agreement with hydrogen peroxide levels reported for coastal sites; nevertheless analysis of H_2O_2 levels with time, in samples with a high H_2O_2 content, reveals that H_2O_2 levels present in rainwater samples decompose readily during the period comprised between collection and analysis, so it was no possible to determine its levels in a suitable way.

On the other hand, 56 samples collected on the roof of the Atmospheric Sciences Centre Building in Mexico City, from April 2 to October 6 of 2001, were preserved only by freezing; in this case, it was found that H_2O_2 levels show a pronounced decay in both standard solutions and samples, therefore there was not any observed preservation effect over samples.
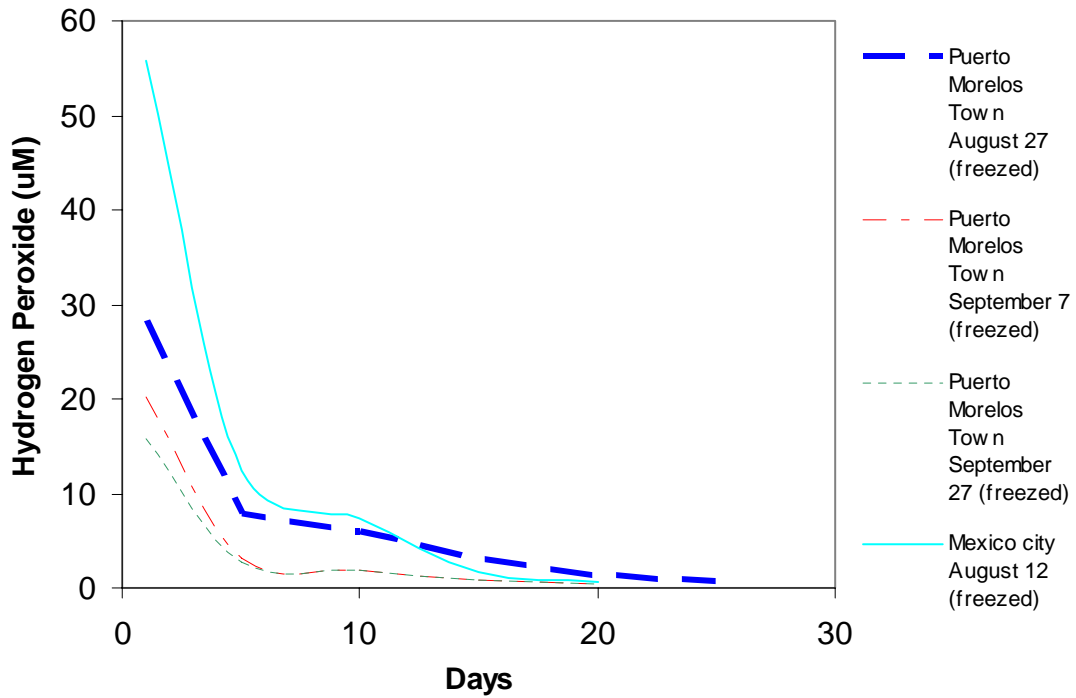
Figure 2. Typical decay curves of hydrogen peroxide levels in rainwater collected in Puerto Morelos Town and on the roof of Atmospheric Sciences Centre Building in Mexico, City, samples were preserved only by freezing
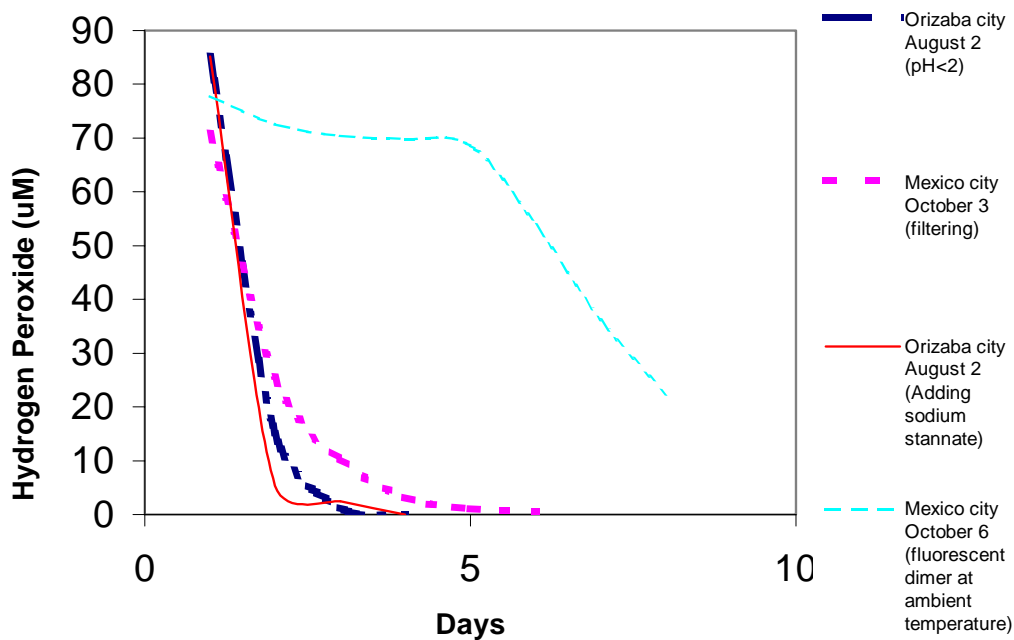

Figure 3 Typical decay curves of hydrogen peroxide levels in rainwater collected on the roof of residential sites in Mexico, City; and Orizaba, City, samples were preserved by filtering, acidification, adding sodium stannate and forming fluorescent dimmer and storing it at ambient temperature

Results showed an average H_2O_2 concentration of 15.24 μM, ranging from 1.83 to 59.46 μM. Typical decay curves in both cases (Puerto Morelos Town and Mexico City) are shown in Figure 2. In these samples, a rather fast initial decay was observed, followed by a considerably
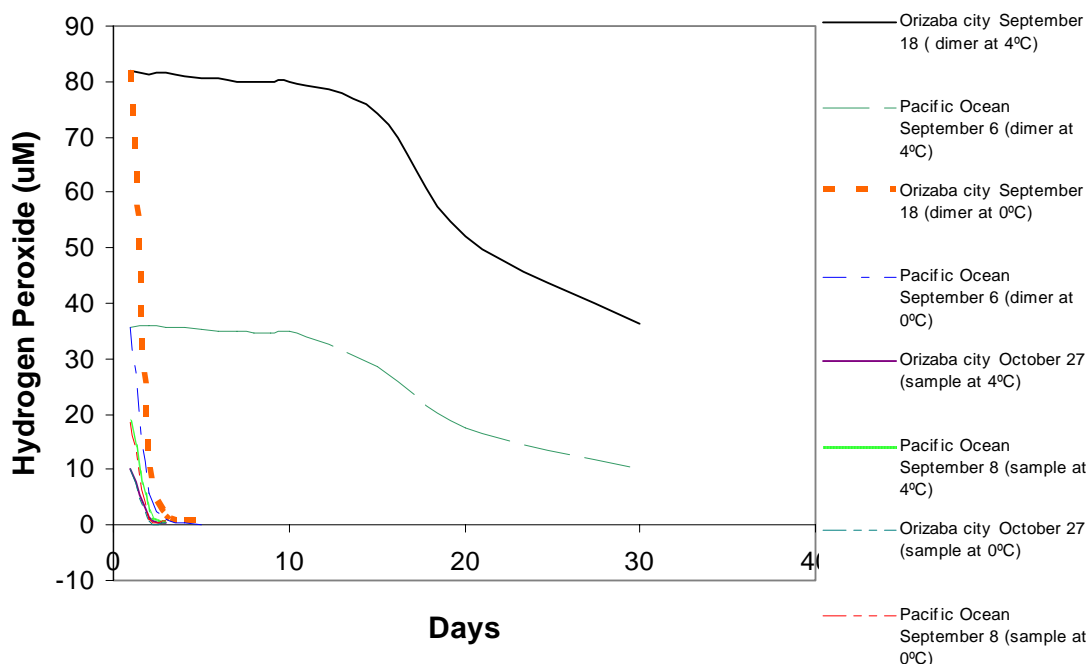
Figure 4   Typical decay of hydrogen peroxide levels in rainwater collected on the roof of a residential house in Orizaba, City and at board of Oceanographic Ship "PUMA" in Tropical Pacific Ocean, samples and their fluorescent dimmer were preserved by storing at 4ºC or at 0ºC

slower decomposition until an almost constant value is reached (or a plateau value). As a result, it was necessary to study the decay of H_2O_2 levels using different preservation methods, before the next sampling period. Deng and Zuo (1999) established that H_2O_2 levels do not decrease with time in filtered samples; however, 55 samples collected on the roof of a residential site in Mexico City from March 24 to October 6 of 2001 were preserved by filtering, and it was observed that filtering does not exert any preservation effect over H_2O_2 levels of samples and standard solutions (Figure 3). Results show an average H_2O_2 concentration of 20.88 μM, ranging from 2.55 to 71.2 μM.

In addition, Ortíz *et al.* (2000) found that more than 70% of the peroxides collected in acidified rainwater samplers (pH<2) are present after 40 hours of their collection, at dark and ambient temperature. While, Sauer *et al.* (1997) proposed to use sodium stannate (J.T. Baker) to preserve the samples for H_2O_2 determination. 44 samples collected in a residential site in Orizaba City from June 8 to October 27 of 2001 were preserved adding nitric acid to obtain a pH of 2, and adding sodium stannate (J.T. Baker). Results showed an average H_2O_2 concentration of 18.6 μM, ranging from 1.73 to 86.9 μM. Figure 3

shows that neither nitric acid nor sodium stannate exert any preservation effect over hydrogen peroxide levels present in rainwater samples.

Several authors (Keuken *et al.*, 1988; Olszyna *et al.*, 1988; Kelly *et al.*, 1985) report that in remote sites, samples stabilized with p-hydroxyphenylacetic acid, can be conserved during several days at ambient conditions. In 35 samples obtained at Atmospheric Sciences Centre Building, in Mexico City from August 3 to October 6 of 2001, it was observed that fluorescent dimmer stays stable until 5 or 6 days after its formation; after 6th day, decay is higher in samples than standard solutions (Figure 3). Results show an average H_2O_2 concentration of 19.24 μM, ranging from 2.37 to 77.92 μM. Similar decay patterns were observed in all samples collected. One additional method assessed was storing samples and its fluorescent dimmer in a cool site at 4ºC or freezing at 0ºC. 40 samples were collected in Orizaba City from June 8 to October 27 of 2001, and on board of Oceanographic Ship "PUMA", in Tropical Pacific Ocean, from May 18 to September 8 of 2001; rainwater samples and their fluorescent dimmer were stored at 4ºC or freeze up. Figure 4 shows a comparison of hydrogen peroxide decay

content in rainwater using cooling or freezing of fluorescent dimmer as sample preservation method. It can be observed that freezing both sample and fluorescent dimmer do not preserve hydrogen peroxide levels. Results show an average H_2O_2 concentration of 15.46 μM, ranging from 1.51 to 82.7 μM. On the other hand, storing at 4ºC does not exert a preservation effect on samples, but assure a minimal decrease in H_2O_2 levels in the case of fluorescent dimmer, giving a time period of 10 days after collection for their determination by fluorescent analysis.

An additional test was performed in order to determine the minimum collection time between fractions from same precipitation event, and to assure the minimal possible degradation in H_2O_2 levels present in rainwater. Test consisted of forming the fluorescent dimmer at different times after collection. Results show a variation of 11, 19.8 and 46.4 %, if dimmer is formed at 0.5, 1 and 4 hours after collection sample. Therefore, to assure a variation less than 10%, during sequential samplings, rainwater fractions must be taken each 15 minutes, forming fluorescent dimmer immediately and storing it at dark and 4 ºC.

CONCLUSIONS

We propose a sampling protocol for H_2O_2 levels in rainwater, by taking rainwater samples each 15 minutes during sequential sampling for an individual rain event, forming fluorescent dimmer on-site immediately after sample collection, and storing at 4ºC and dark. This procedure, give us a margin of 10 days to perform sample analysis, guarantying a minimal decomposition of H_2O_2 in rainwater samples (approximately 10%) and permitting to perform sampling campaigns even in remote sites. The other methods evaluated do not exert any preservation effect over H_2O_2 levels in rainwater samples.

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